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RESEARCH

Process standardization and kinetics of ethanol driven biodiesel production by transesterification of ricebran oil

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Abstract In this study, trans-esterification of rice bran oil employing a heterogeneous catalyst like CaO has been conducted in a batch reactor with ethanol. The optimal set of various critical reaction parameters are found to be temperature of 70 °C, reactant molar ratio 9:1, agitation speed of 600 rpm, catalyst mount of 3 wt % to maximize the biodiesel yield. For the heterogeneous system possibly influenced by reaction and pore diffusion, the controlling regime has been found based on the experimental data and well established theoretical estimations. The kinetic model along with the relevant parameters viz., reaction order, rate constants and Arrhenius parameters have been estimated.

Keywords Trans-esterification · Biodiesel · Kinetics · Controlling regime · Process standardization

List of symbols

Variables

a_m	Specific surface area of catalyst (m^2/gm)
A	Frequency factor (min^{-1})
c_A	Concentration of triglyceride in liquid phase (mol/l)
c_{A_0}	Initial concentration of triglyceride in liquid phase (mol/l)
$c_{A,s}$	Concentration of triglyceride on the interfacial solid liquid area (mol/l)
c_B	Concentration of ethanol in liquid phase (mol/l)
c_R	Concentration of FAEE in liquid phase (mol/l)
C	Integration constant
D	Molecular diffusion coefficient (m^2/s)
D_{eff}	Effective diffusion coefficient (m^2/s)
E_a	Activation energy (KJ/mol)
k	Pseudo-first order reaction rate constant (min^{-1})
k_{ad}	Ethanol adsorption rate constant (min^{-1})
k_{app}	Apparent process rate constant (min^{-1})
$k_{s,A}$	Triglyceride mass transfer coefficient towards catalyst surface (m/min)
$k_{mt,A}$	Volumetric triglyceride mass transfer coefficient (min^{-1})
m_{cat}	Mass of heterogeneous catalyst (g)
M	Molecular weight of solvent
Q	Instantaneous concentration of adsorbed ethanol (mol/gm)
Q_{max}	Maximum concentration of adsorbed ethanol (mol/gm)
$(-r_A)$	Rate of triglyceride consumption (mol/(l min))
$(-r_B)$	Rate of ethanol consumption (mol/(l min))
R	Gas constant (J K^{-1} mol^{-1})
R_p	Catalyst particle radius (m)
t	Time (min, s)
T	Temperature (K)
Th	Thiele modulus
V	Volume of reaction mixture (cm^3)
V_m	Molal volume of solute at normal boiling point (cc/g mol)
x	Association parameter of solvent
X_A	Degree of triglyceride conversion

Greek symbols

ε_p	Catalyst particle porosity
τ_p	Catalyst particle tortuosity

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η Viscosity of solution (cp)
θ Fraction of the catalyst available active specific surface

Introduction

Rapid industrialization and increasing population at a global level has led to a tremendous upswing in the energy utilization [1, 2]. Hence the focus has been shifted in employing renewable energy resources due to the anticipated exhaustibility of the fossil reserves besides the growing concern for environmental quality. Biodiesel has become the researchers' spotlight for some time now due to its significant attributes like green and non-toxic nature leading to significant reduction in greenhouse gases, renewability and biodegradability [3, 4].

Conventionally, biodiesel is produced by transesterification of triglyceride feedstock (vegetable oils/animal fats/waste cooking oils) with methanol or other short chain alcohols in the presence of a catalyst. Many studies have been reported on this reaction employing various homogeneous and heterogeneous catalysts with different types of oils viz., palm, sunflower, rapeseed, soyabean oils. Heterogeneous catalysts like zeolites, metal oxides, heteropolyacids, hydrotalcites are preferred to the homogeneous catalysts like KOH or NaOH due to their reusability, eco-friendly nature and easy separation of products [5–8]. On the other hand, the homogeneous catalysis route though relatively rapid and result in higher yields, is not recommended due to commercial reasons as it demands high quality crude oils and an expensive and toxic downstream processing due to undesired side reactions like saponification and hydrolysis occurring. Hence there has been a growing impetus on the heterogeneous synthesis, identifying novel and effective catalysts and cost effective feedstock as the main hurdle in the commercialization of biodiesel production by transesterification reaction has been the high cost of raw materials which contributes to 70 % of total cost [9]. Various research studies have been reported on this topic like process standardization with reference to various critical parameters like nature of vegetable oil and alcohol, reactant mole ratio, nature and amount of catalyst, reaction time, agitation rate and temperature and employing different reaction conditions like microwave irradiation, ultrasonic assisted and supercritical conditions to maximize biodiesel yield and reaction rate [10–19].

In this work, biodiesel synthesis has been carried out in a batch reactor using ricebran oil and ethanol in the presence of heterogeneous catalyst, CaO. Various properties of Rice Bran oil have been listed in Table 1. The influence of various process parameters has been investigated to maximize the biodiesel yield and kinetic studies have been conducted at optimal conditions to estimate the rate constants. Ricebran oil has been selected for our study as it is derived from agricultural waste which is abundantly available in most of the rice producing countries and has a significant potential as an alternative cost-effective feedstock when compared to those derived from cereal or seed sources like sunflower, soyabean, canola etc. [20–23].

Table 1 Properties of rice bran oil

Property	Refined rice bran oil
Moisture (%)	0.1–1.15
Density	0.913–0.920
refractive index	1.4672
Saponification value	187
Free fatty acids (%)	0.15–0.2
Kinematic viscosity @ 40 °C (cSt)	43.52
Cetane number	50.1
Cloud point (°C)	13
Pour point (°C)	1
Flash point (°C)	316
Calorific value (MJ/kg)	41.1

Materials and methods

The reactants for the transesterification reaction viz., rice bran oil (100 % pure. Priya brand), ethanol (99 % pure) and extra pure CaO catalyst (size <150 nm) are procured from Hi-Media Labs, Hyderabad and are used as is. The experimental set-up (Fig. 1) employed for the reaction consists of three necked borosil glass reactor of 1 l capacity immersed in a constant temperature oil bath with a propeller inserted at the centre to agitate the reaction mixture. The reactants of predetermined quantities are fed to the reactor and the reaction is conducted to produce the desired product of biodiesel. The reaction scheme for the transesterification reaction is shown in Fig. 2. Biodiesel yield is estimated using a Gas Chromatograph (Agilent make, 7820A model with HP88 column) fitted with HP88 column. The conditions employed for GC analysis are FID temperature: 260 °C; Oven temperature initially at 125 °C raised to 145 °C at a rate of 8 °C/min and then maintained at that temperature for 26 min after which it is increased to 220 °C at a rate of 2 °C/min and then kept steady for 1 min. 0.2 µl of the product sample from biodiesel rich layer after quenching it in an ice bath to arrest any further reaction is injected along with solvent hexane into GC to get various peaks from which biodiesel yield is estimated. Experiments have been conducted to study the influence of

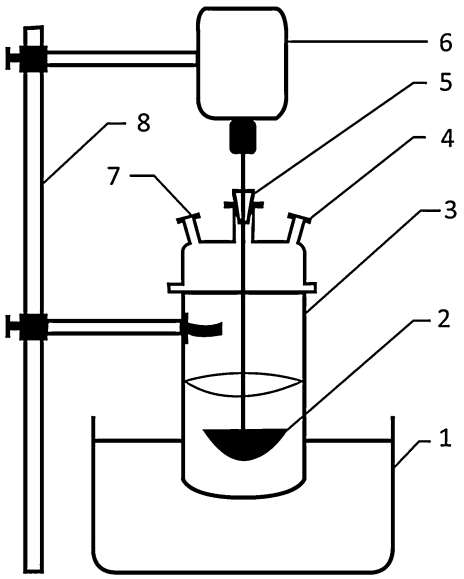


Fig. 1 The apparatus for transesterification reaction: *1* digitally controlled water bath, *2* impeller blade, *3* three necked glass flask, *4* inlet for reactants, *5* rubber cork, *6* stirrer, *7* inlet for temperature measurement, *8* retort stand

various critical parameters viz., reaction temperature (50, 60, 70 and 80 °C); reactant mole ratio (ethanol to oil ratios of 6:1, 9:1 and 12:1); agitation speed (400, 600 and 800 rpm); catalyst weight percent (1.5, 3, 4.5 and 6 %) and reaction time (30, 60, 90 and 120 min) on biodiesel yield.

Results and discussion

Effect of reaction temperature

Temperature has been reported to be one of the critical parameters in the transesterification reaction for biodiesel synthesis. Experiments have been carried out at three different temperatures of 50, 60 and 70 °C keeping all other parameters viz., agitation speed, catalyst amount, reactant

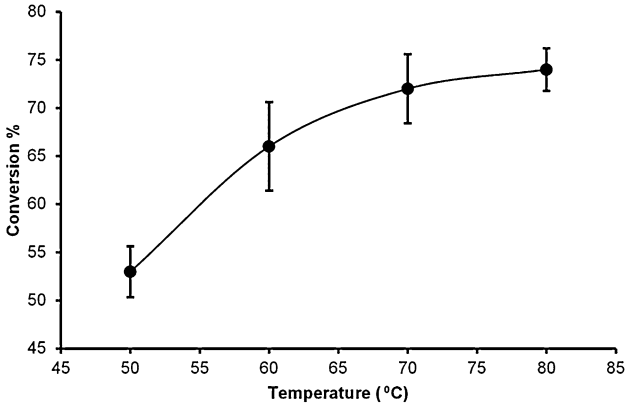


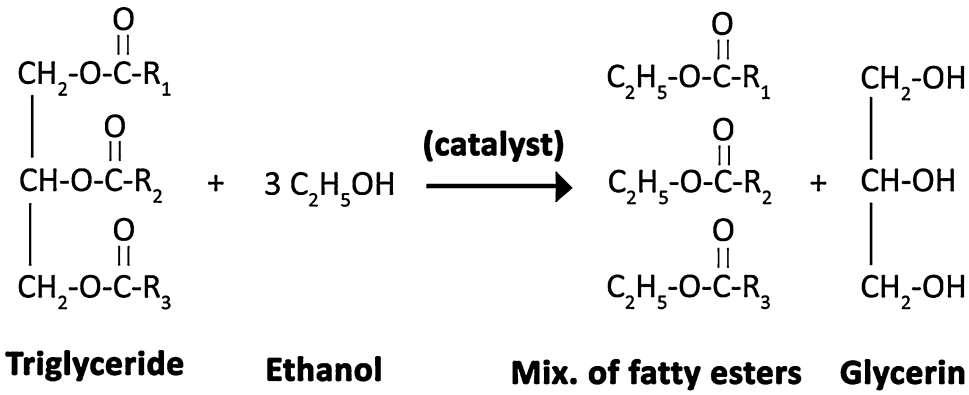
Fig. 3 Influence of temperature on conversion at 600 rpm, 3 wt % catalyst, ethanol/oil molar ratio 9:1, reaction time 2 h

molar ratio constant. The results are given in Fig. 3 which a positive influence of temperature on the biodiesel yield giving more than 70 % at 70 °C. Our results are found to be in agreement with those reported by Wu et al. [24, 25].

Effect of molar ratio of reactants

In order to examine the effect of molar ratio of ethanol to rice bran oil on the yield, reactions are carried out using three different mole ratios 6:1, 9:1, 12:1 keeping all other parameters constant and the results obtained are shown in Fig. 4. In trans-esterification reaction, 1 mol of vegetable oil reacts with 3 mol of ethanol to give 3 mol of biodiesel and 1 mol of glycerol and this was a reversible reaction. So, excess of any of the reactant (more than stoichiometric ratio, 3:1) should shift the equilibrium to the right pushing the forward reaction achieving enhanced yield of 72 % till 9:1 mole ratio. Yield was found to decrease to 64 % at 12:1 mol ratio due to the relative decrease in the catalyst amount vis-a-vis the reaction mixture and hence the possible triggering of reverse reaction by the enhanced formation of glycerol which reacts with biodiesel formed reducing its yield to 64 % [16].

Fig. 2 Transesterification reaction



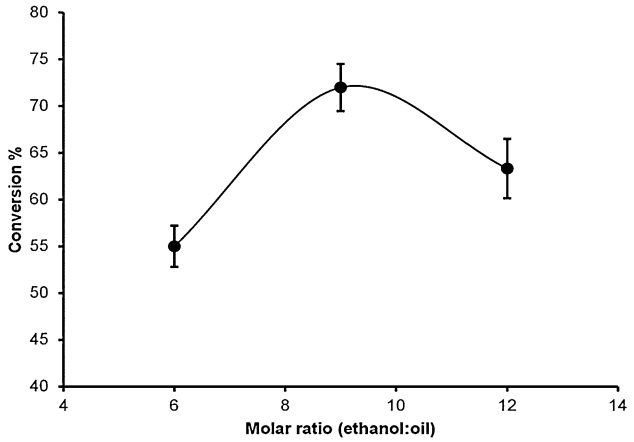


Fig. 4 Influence of reactant molar ratio on conversion at 600 rpm, 3 wt % catalyst, temp. 70 °C, reaction time 2 h

Hence 9:1 is found to be the optimal mole ratio of ethanol to oil to achieve maximum yield. Similar results have been reported by Wang et al. [26].

Effect of agitation speed

Experiments have been conducted at various stirrer speeds of 400; 600 and 800 rpm to understand its influence on the biodiesel yield maintaining all other parameters constant. Figure 5 shows the results of this study according to which it was clear that 600 rpm was optimum giving maximum yield of biodiesel, 71 %. The results employing two different catalyst amounts 3 and 6 % were shown in the Figure. It was found that the 600 rpm was optimum for both the cases and that 3 % catalyst gave relatively higher yields when compared to 6 %. The existence of optimum rpm could be explained by the swirling effect at higher speeds in unbaffled vessels that leads to concentration of solid instead of the desired suspension [27]. This effect of swirling would be more pronounced with higher catalyst amount which also would increase the solution viscosity reducing the reactant mobility and hence the yield as is evident from the Fig. 5.

Effect of catalyst amount

To understand the effect of catalyst amount on the biodiesel yield, experiments were conducted using various amounts of 1.5 %. 3, 4.5 and 6 % on weight basis. The results are given in Fig. 6 below according to which 3 % was the optimum amount of catalyst that gave highest biodiesel yield of 72 %. From the plot, it is clear that the biodiesel yield increased with amount of catalyst up to certain extent i.e., 3 % beyond which the yield is observed to decrease. This can be attributed to various factors like increase in solution viscosity that makes stirring ineffective, increasing importance of mass transfer than the catalyst amount under alkaline conditions and more pronounced swirling effect at higher speeds. Similar results have been reported by, Lin et al. [28] and Lueng-naruemitchai et al. [29].

Effect of reaction time

The transesterification reaction under optimal conditions as above was conducted for 2 h with samples taken every 15 min i.e., at intervals of 15, 30, 45, 60, 75, 90, 105 and 120 min. The results obtained are shown in the Fig. 7 according to which the biodiesel yield increased with time up to 90 min achieving 70 % yield after which there is no significant change in the yield as the reaction could have reached near equilibrium conversion. It is also evident from the plot that it required about 30 min to achieve most conversion after which there is only a slight increase.

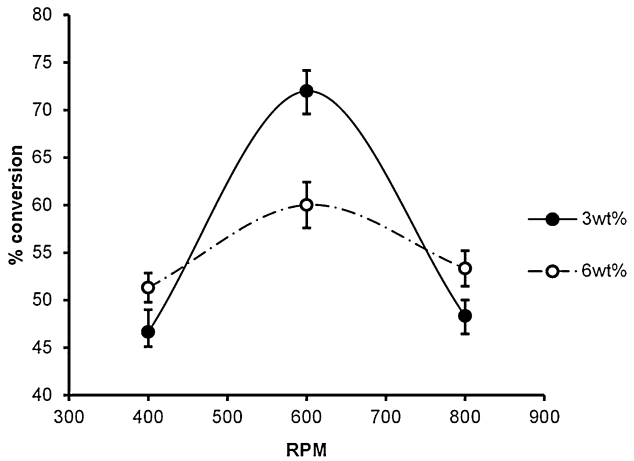


Fig. 5 Influence of agitation speed on conversion at 70 °C, reaction time 2 h, 3 wt % and 6 wt % catalyst, 9:1 molar ratio of ethanol to oil

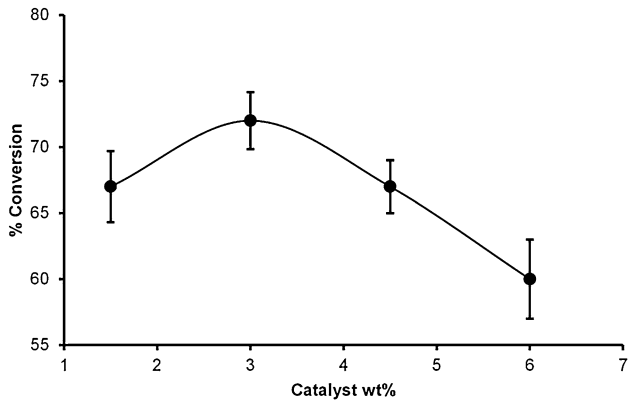


Fig. 6 Influence of catalyst wt % on conversion at 600 rpm, ethanol/oil molar ratio 9:1, temp. 70 °C, reaction time 2 h

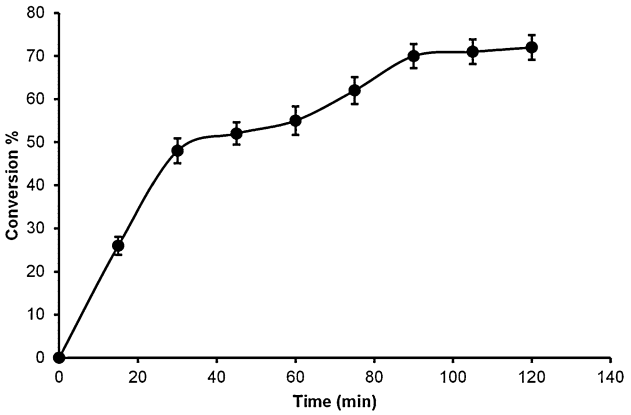


Fig. 7 Influence of reaction time on conversion at 600 rpm, ethanol/oil molar ratio 9:1, temp 70 °C, 3 wt % catalyst

Similar trends have been reported on the influence of time on percent conversion [30–32].

Recyclability studies

The biodiesel synthesis at the optimal conditions of 70 °C, 90 min; 3 wt % catalyst; 9:1 mol ratio of reactants (ethanol to oil) and the agitation speed of 600 rpm has been conducted up to three cycles by recycling the CaO catalyst after regenerating through filtration and calcination. The biodiesel yield of 72 % has been successfully achieved in all the three cycles within a range of 5 %. This reinforces the selection of calcium oxide as a stable catalyst in the transesterification reaction without undergoing major physico-chemical changes. Lee et al. [33] too observed that CaO and other mixed oxides were stable up to multiple cycles in the esterification and transesterification reactions.

Reaction kinetics

Theoretical approach

The overall transesterification of rice bran oil can be represented in following stoichiometric equation:

$$A + 3B \leftrightarrow 3C + D \quad (1)$$

where A is triglyceride, B is ethanol, C is Fatty acid ethyl ester and D is glycerol.

The transesterification reaction by heterogeneous catalyst occurs in a three phase system with two immiscible liquid phases (Rice bran oil and Ethanol) and solid (calcium oxide) as catalyst. Along with the transesterification, some side reactions also occur such as saponification of glycerides, ethyl esters and neutralization of fatty acids by catalyst. The following assumptions were used to model the process of transesterification.

Assumptions:

1. The transesterification reaction occurs between glycerides and ethoxide ions adsorbed on catalyst surface.
2. The mass transfer rate of ethanol towards catalyst surface and its adsorption rate onto surface of catalyst do not limit the overall rate of reaction.
3. The mass transfer rate of glycerides towards catalyst surface influences the overall reaction rate in the initial reaction period.
4. The mass transfer rate of glycerides towards the catalyst surface determines its adsorption rate onto active sites of catalyst surface during the initial reaction period.
5. Ethanol adsorption onto catalyst surface follows pseudo-first order kinetics.
6. When the external mass transfer limitation gets negligible in the later reaction period, the rate of reaction between triglycerides and ethoxide ion influences the overall reaction rate.
7. The reaction of triglyceride follows pseudo-first order reaction.
8. The rate of desorption of transesterification products from catalyst surface and their mass transfer rates into reaction mixture do not influence overall reaction rate.
9. The internal diffusion rate will not influence the transesterification reaction.
10. The reaction mixture is assumed to be homogeneous throughout i.e., its composition and catalyst distribution are uniform since the reaction is performed in a batch reactor.
11. The neutralization of free fatty acids is assumed to be negligible since the refined rice bran oil used in the reaction had around 0.15–0.2 % of free fatty acids.

The process of transesterification catalyzed by heterogeneous catalyst contains several steps, hence rate limiting step should be determined by comparing their rates. The adsorption rate of ethanol onto the catalyst surface area is equal to the rate of its concentration increase on the catalyst surface.

$$\frac{m_{cat}}{V}\frac{dQ}{dt} = k_{ad}(Q_{max} - Q)\frac{m_{cat}}{V} \quad (2)$$

where Q and Q_{max} are the instantaneous and maximum adsorbed ethanol concentrations on the surface of catalyst, k_{ad} is the rate constant for ethanol adsorption, m_{cat} is the mass of catalyst, V is the volume of reaction mixture, and t is the time.

For mass balance of ethanol on surface of catalyst, rate of ethanol depletion in the bulk phase is determined by the

mass transfer of ethanol from bulk phase to active sites of catalyst surface and the rate of adsorption on the catalyst surface.

$$(-r_B) = \left(-\frac{dc_B}{dt}\right) - \frac{m_{cat}}{V}\frac{dQ}{dt} \quad (3)$$

where c_B is ethanol concentration adsorbed in the liquid phase and $(-r_B)$ is the rate of ethanol depletion reaction rate.

Since ethanol depletion rate is equal to rate of formation of Fatty acid ethyl esters (FAEE):

$$(-r_B) = \frac{dc_R}{dt} \quad (4)$$

where c_R is the FAEE concentration in the liquid phase and the Eq. (3) can be transformed into

$$\frac{dQ}{dt} = \left[\left(-\frac{dc_B}{dt}\right) - \frac{dc_R}{dt}\right]\frac{V}{m_{cat}} \quad (5)$$

From the assumptions (3), (4) and (7) the mass transfer rate of triglyceride is equal to its reaction rate:

$$(-r_A) = -\frac{dc_A}{dt} = k_{s,A}.\theta.a_m.\left(c_A - c_{A,s}\right).\frac{m_{cat}}{V} = k.c_{A,s} \quad (6)$$

where $k_{s,A}$ is the mass transfer coefficient of triglyceride, θ is the fraction of the available active surface area of catalyst, a_m is the active surface area of catalyst, c_A and $c_{A,s}$ are triglyceride concentrations in liquid phase and adsorbed on catalyst surface per liquid phase volume respectively and k is the reaction rate constant of pseudo-first order reaction.

Introducing a new term, volumetric triglyceride mass transfer constant $k_{mt,A}$ as follows:

$$k_{mt,A} = k_{s,A}.\theta.a_m.\frac{m_{cat}}{V} \quad (7)$$

Now the Eq. (6) becomes

$$(-r_A) = k_{mt,A}.\left(c_A - c_{A,s}\right) = k.c_{A,s} \quad (8)$$

By rearranging the equation, easily measurable c_A is used to express not measurable $c_{A,s}$:

$$c_{A,s} = \frac{k_{mt,A}}{k_{mt,A} + k}.c_A \quad (9)$$

This can be rearranged to:

$$-\frac{dc_A}{dt} = \frac{k.k_{mt,A}}{k_{mt,A} + k}.c_A \quad (10)$$

which could be represented as

$$-\frac{dc_A}{dt} = k_{app}.c_A \quad (11)$$

where k_{app} is the apparent rate constant which is a function of both mass transfer and chemical reaction rate. From Eq. (10) there are possibilities of two extreme situations during transesterification reaction. Based on assumption (4), if $k_{mt,A} \ll k$ in the initial reaction period:

$$k_{app} = k_{mt,A} \quad (12)$$

Which means in the initial reaction period, the mass transfer rate limits the overall reaction rate which and also depends on amount of catalyst according to Eq. (7) i.e.,

$$-\frac{dc_A}{dt} = k_{mt,A}.c_A \quad (13)$$

In later stages of reaction, the adsorbed ethanol concentration decreases on catalyst surface and at the same time fraction of active catalyst surface available for triglyceride adsorption and volumetric triglyceride mass transfer coefficient increase. When $k_{mt,A} \gg k$:

$$k_{app} = k \quad (14)$$

Which means the overall rate depends on the chemical reaction rate between adsorbed ethanol and triglyceride molecules i.e.,

$$-\frac{dc_A}{dt} = k.c_A \quad (15)$$

The triglyceride concentration can be expressed in terms of conversion as follows:

$$c_A = c_{A_0}(1 - X_A) \quad (16)$$

Now, Eq. (11) can be written as

$$\frac{dX_A}{dt} = k_{app}(1 - X_A) \quad (17)$$

After integration, following equation is obtained:

$$-\ln(1 - X_A) = k_{app}t + C \quad (18)$$

where C is the integration constant. Hence, both reaction rate and mass transfer follow first order kinetics with a different rate constant ($k_{app} = k$ and $k_{app} = k_{mt,A}$ respectively).

Internal mass transfer limitation

If the internal mass transfer resistance exists, then it will contribute to the reaction rate. This can be verified theoretically by calculating the Thiele modulus. If the value of Thiele modulus is less than 0.4, it implies that the resistance offered by catalyst pores is negligible.

Thiele modulus for a spherical particle is given by

$$\mathrm{Th} = \frac{R_p}{3}\sqrt{\frac{k}{D_{eff}}} \quad (19)$$

where R_p is radius of particle, k is the rate constant of pseudo-first order reaction, D_{eff} is effective diffusion coefficient. In our work the rate constant was found to be 0.0103 min^{-1} and the largest average particle size is

15.3 μm. The effective diffusion coefficient can be calculated by the following equation:

$$D_{\text{eff}} = \frac{D\varepsilon_p}{\tau_p} \tag{20}$$

where D is the molecular diffusion coefficient, ε_p porosity of catalyst particle, τ_p is the catalyst particle tortuosity. The following equation can be used to calculate the molecular diffusion coefficient of triglycerides through ethanol.

$$D = 7.4 \times 10^{-8}\left(\frac{(xM)^{0.5}T}{\eta V_{\text{m}}^{0.6}}\right) \tag{21}$$

where x is the association parameter of solvent (1.5 for ethanol), M is molecular weight of solvent, T is temperature in K, η is viscosity of solution in centipoise, V_{m} is molal volume of solute at normal boiling point in cc/g.mol.

The temperature of best case scenario is 70 °C (343 K), η of the solution is 4.388 centipoise, molecular weight of solvent is 46 g/mol, molal volume of solute is 950.711 cc/g.mol. At these conditions value of D was found out to be 7.849×10^{-7} m^2/s and $D_{\text{eff}} = 1.046^{-7}$ m^2/s, from which we can calculate the value of Thiele modulus which was calculated to be 8.001×10^{-4}. Hence the Thiele modulus is far below its lower limit of 0.4 and hence the internal mass transfer can be neglected.

Experimental approach

From equation (18), the plot of $-\ln(1 - X_{\text{A}})$ vs t are drawn for different reaction scenarios and were compared with first order reaction line, and the corresponding correlation coefficients were found to be 0.9346, 0.9439 and 0.932 for 70, 60 and 50 °C reaction respectively while keeping other reaction parameters same at ethanol/oil molar ratio of 9:1, 600 rpm and 3 wt % catalyst. While comparing with second order reaction, the correlation coefficient was found to be 0.634 (Fig. 8) much lesser than first order assumption. Hence it follows pseudo-first order reaction.

First order rate constants are estimated at three different temperatures of 50, 60 and 70 °C by plotting '$-\ln(1 - X_{\text{A}})$ vs t'. These plots are shown in Fig. 9 and the corresponding k values are 0.0059, 0.0082 and 0.0103 min^{-1} which were employed to calculate the Arrhenius parameters.

$$k = Ae^{\frac{-E_{\text{a}}}{RT}} \tag{22}$$

Activation energy for the reaction, E_{a} and the frequency factor A are estimated using Arrhenius Eq. (19) and making a plot of ln k vs $1/T$ (Fig. 10).

The Arrhenius parameters estimated are

$$E_{\text{a}} = 25.723 \text{ KJ/mol} \quad A = 86.091 \text{ min}^{-1}$$

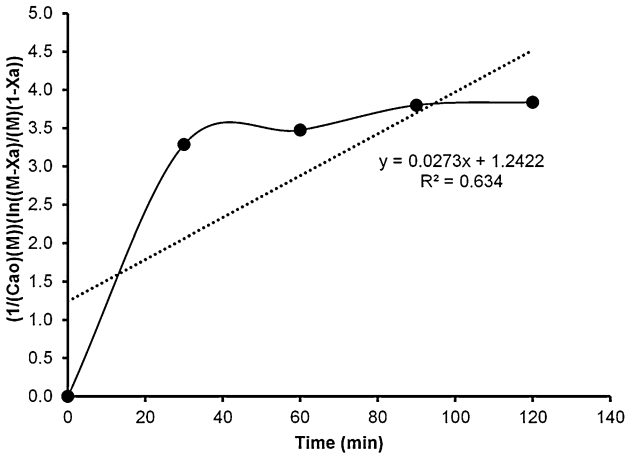


Fig. 8 Second order reaction assumption at 600 rpm, ethanol/oil molar ratio 9:1, temperature 70 °C, 3 wt % catalyst

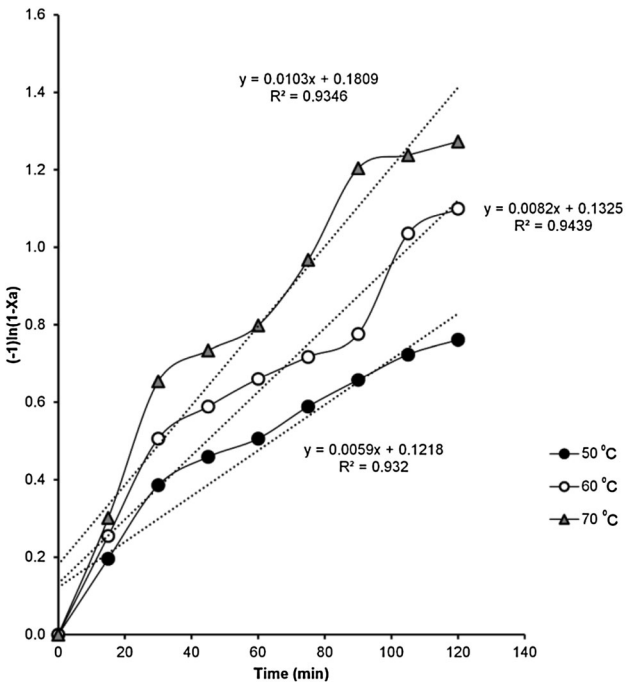


Fig. 9 First order reaction assumption at 600 rpm, ethanol/oil molar ratio 9:1, 3 wt % catalyst and temperatures 50, 60, 70 °C

Conclusions

In this work, biodiesel production through transesterification reaction using ethanol and not so edible and cost-effective oil of rice bran oil has been standardized with reference to various critical parameters viz., temperature, reactant mole ratio, catalyst amount, agitation speed, reaction time to achieve maximum yield. Our studies

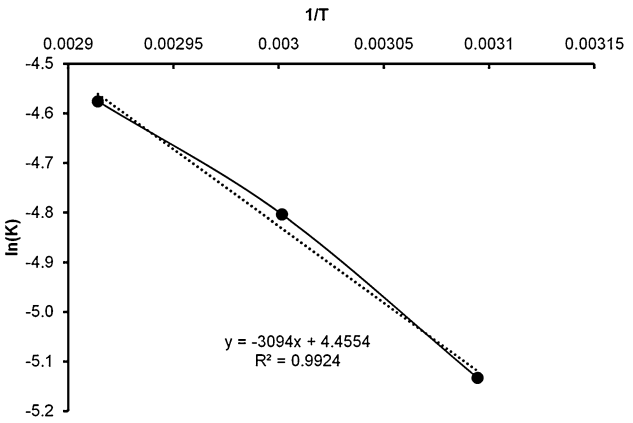


Fig. 10 Arrhenius plot for three temperatures, 50, 60 and 70 °C

indicate that ethanol too can be used in place of methanol as alcohol in the reaction to achieve reasonable yields. The kinetic studies conducted show that the transesterification reaction is very fast with major reaction completed during the initial 30 min after which there is only a marginal increase up to 90 min. For the multiphase reaction, the controlling regime is estimated from experimental and theoretical validations and then a suitable kinetic model has been formulated that fits well with the experimental data. All the kinetic parameters have been estimated. In future, this reaction has to be further studied in identifying other critical parameters like pressure, reactor configuration, vapour phase reaction, mixing intensity with various impellers etc.

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